

KLINGER & GRIFFITH

18 JUN 1982

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AD A117346

Fluoropolymer Barriers to Stress Corrosion in Optical Fibers

Liliana Klinger
USA CECOM, Ft. Monmouth, NJ 07703

James R. Griffith
Naval Research Laboratory
Washington, DC 20375

Organic polymer coatings play a critical role in determining the overall performance of optical fibers. They protect the very fine silica glass core from abrasive damage and environmental effects such as stress induced corrosion. In addition they act as a buffer in reducing the sensitivity of the optical fiber to microbending loss¹. Military requirements for optical fiber coatings are more stringent than those for coatings used in commercial applications. No more than two or three coatings may be applied to the fiber so that it remains light enough for possible use in helicopter payout and missile tracking systems. Application of the coating must be done in line with the drawing of the glass fiber; thus low viscosities (10^3 - 10^4 cps), rapid solidification and fast crosslinking reactions are required. Ultraviolet² cures are preferable, but rapid thermal cures are possible².

Stress induced corrosion by H_2O is associated with stress concentrations at surface flaws under deformation. The only way to protect the glass fiber against stress corrosion is to prevent the buildup of H_2O and OH at the fiber surface. Polymer coatings for optical fibers must thus be designed to reduce permeation of H_2O through the polymer matrix. Moisture may permeate through the polymer coating(s) while it is being stored under tension (wound on drums) or during deployment on hydrous terrain. The process of permeation of H_2O through a polymer film involves, wetting of the polymer surface, sorption of H_2O into the polymer matrix, diffusion through the film along a concentration gradient and desorption of H_2O from the polymer surface^{3,4}. Incorporation of fluorine into the polymer chain has been found to reduce surface wettability and sorption of H_2O ⁵. In addition, halogenated polymers have been found to have amongst the lowest moisture vapor permeabilities of all polymers (see Table 1)³.

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Two fluorinated polymers were investigated as possible coatings for optical fibers; a heat cured fluoroepoxy (see Fig. 1) and a photocured fluoroacrylate (see Fig. 2). In addition to barrier properties such factors as flexibility, strength and modulus must be considered in designing a suitable coating.

Fluoroepoxy resin is synthesized by mixing the diglycidyl ether with bis- γ -aminopropyl (tetramethyl disiloxane) at 50°C until both reactants become mutually soluble. Films were then solvent cast using Freon TF solvent and cured at 80°C.

Fluoropolyolacrylate is a long chain monomer containing aromatic and oxerane rings; photopolymerization occurs through pendant ester groups. Films were solvent cast using Freon TF, in a nitrogen atmosphere and subsequently exposed to ultraviolet radiation.

In both systems fluorine is incorporated into the polymer chain as fluoromethyl groups. The C_6 fluoroepoxy has an additional fluorinated hexane attached to the aromatic ring. The long chain adds flexibility whereas the aromatic ring gives strength and resiliency.

Determining the effects of chemical and physical structure on moisture vapor permeability of these films requires balancing several conflicting factors; these include effects of polar groups, fluorinated substituents, symmetry and segmental mobility. Polar groups which improve adhesion to glass and prevent buildup of H_2O at the interface also increase moisture vapor permeability. This is due to strong localized interactions between the small polar H_2O molecule and polar groups within the polymer⁴. Although the silicone amine curing agent reduces the fluorine content and thus barrier properties of the epoxy film, it acts in a manner similar to silane coupling agents in improving adhesion to glass. Both low moisture vapor permeability and good adhesion are important factors in preventing stress corrosion of the optical fiber.

Wettability studies are reported in terms of the contact angle, θ , H_2O , made by triply distilled water on fluoroepoxy + fluoropolyolacrylate films. Contact angles were measured at ambient temperature on an NRL contact-angle goniometer. Critical surface tensions of wetting γ_c were determined from contact angles of a series of n-alkanes. The cosines of the contact angles of the n-alkanes were plotted against the surface tensions γ_{LV} of these liquids and the intercept of the resultant straight line at $\cos \theta = 1$ ($\theta = 0^\circ$) is denoted as γ_c (see Fig. 3).



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Moisture vapor permeability was determined using the cup method (Gardner-Park Permeability Cup - ASTM Standard D1653-72) maintained in a relatively anhydrous environment ($15\% \pm 1$ humidity) at $22^\circ\text{C} \pm 1$. A thin polymer film was placed over an aluminum cup containing 7 ml of distilled H_2O ; the entire system was weighed and placed in a dessicator. It was subsequently weighed every 24 hours to determine how much H_2O had permeated the polymer sample. Weight was plotted against time; when the system reaches a steady state all points lie on a straight line (see Fig. 4).

Preliminary results (see Table 2) indicate that despite the difference in contact angle and surface tension, moisture vapor permeability of the two films remain about the same. As mentioned earlier, permeability is a composite quantity governed by two independent parameters, diffusion and solubility of H_2O in the polymer. Sorption studies on various fluoroacrylate and fluoroepoxy systems indicate that the acrylates absorb less H_2O than the epoxies⁶. Diffusion properties have as yet not been determined. This implies that the low moisture vapor permeability of the polyfluoropolyolacrylate film is in part due to low H_2O absorption given the superior surface properties of the fluoroepoxy film.

Polymer coatings can be designed to reduce stress concentrations at surface flaws as well as sensitivity to microbending loss. (Small external forces due to an irregular surface are sufficient to cause lateral deformations, mode coupling and optical loss.) The elastic or relaxation modulus E of the polymer is a good indicator of how effective the coating is in protecting the clad fiber from these effects. In order to determine their elastic modulus E and glass transition temperature T_g , dynamic mechanical tests were performed on the fluoroepoxy (see Fig. 5) and polyfluoropolyolacrylate polymer films (see Fig. 6) using a Rheo-Vibron DDV-II. It has been observed that coatings with relaxation modulus values less than 10^8 dynes/cm² are effective in protecting the glass fiber from stress concentrations and reducing microbending loss.

Both fluoroepoxy and polyfluoropolyolacrylate polymers respond in a similar manner to changes in temperature under the applied oscillatory force of the Rheo-Vibron. This is probably due to similarities in chemical structure. At ambient temperature (22°C) the elastic modulus of the fluoroepoxy polymer is 2×10^{10} dynes/cm², while that of the polyfluoropolyolacrylate is 4×10^{10} dynes/cm². The glass transition or drop in modulus of both systems, to about 10^8 dynes/cm², occurs at about 50°C . It is possible to reduce the temperature of the glass transition and the modulus below T_g by reducing the crosslink density of the polymer network.

In order to reduce the crosslink density of the polyfluoropolyolacrylate, it would be necessary to react some of the pendant OH groups with nonreactive chemical groups (such as dimethyl sulfate or pentafluorophenylisocyanate) before attaching the ester

group ($-O-\overset{\text{H}}{\underset{\text{O}}{\text{C}}}-\text{C}=\text{C}$) that participates in the crosslinking reaction. Since this procedure would also reduce the modulus below T_g , we would obtain a polymer with a modulus less than 10^8 dynes/cm² at ambient temperatures, as required.

In designing a coating system for optical fibers it is necessary to strike a balance between two factors: a soft compliant enclosure that acts as a buffer in masking the nonuniform surface of the glass and a hard enclosure to act as a stiffener and make the fiber resistant to the environmental surface. These requirements are best suited by using a photocured polyfluoropolyolacrylate of reduced crosslink density as a primary coating and the high modulus fluoroepoxy resin as a secondary coating. Although it is possible to lower the glass transition and modulus of the fluoroepoxy system, the longer cure times required for heat curing systems, make them less attractive as a primary coating. Also the superior surface properties of the fluoroepoxy suggest themselves for use as an external coating.

References

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Table 1

Permeability Properties of High Barrier Polymers

| Polymer | Polymer Class | ^b Water |
|--------------------------------|---------------|--------------------|
| Polyvinylidene chloride | Halogen | 0.2 |
| Lopac ^a | Nitrile | 5.0 |
| Barex | Nitrile | 6.1 |
| Cycopac | Nitrile | 5.0 |
| Saran Wrap | Halogen | 0.5 |
| Epoxy (bisphenol A/amine cure) | Thermoset | 4.0 |
| Kel-F (PCTFE) | Halogen | 0.3 |
| Trogamid T | Polyamide | 5.2 |
| Kynar (PVDF) | Halogen | 1.0 |
| Nylon 69-nylon 610 | Polyamide | 6.0 |
| Polyethylene terephthalate | Polyester | 2.0 |
| Phenoxy | Condensate | 4.5 |
| PVC (rigid) | Halogen | 2-3 ^c |

^aAcrylonitrile-styrene copolymer used for manufacturing Monsanto Cycle-Safe containers (70% AN).

^bg/24 hr/100 in.²/mil at 100°F (100% RH).

^cDepends on exact compound formulation.

Table 2
Surface Properties and Permeability

| Film (3 mil) | H ₂ O | c | MVP |
|----------------------|------------------|-----------|--------------------------------|
| | | (dyne/cm) | g/(25 cm ² -24 hrs) |
| Fluoroepoxy | 81° | 18.3 | .033 |
| Fluoropolyolacrylate | 71° | 25.4 | .031 |

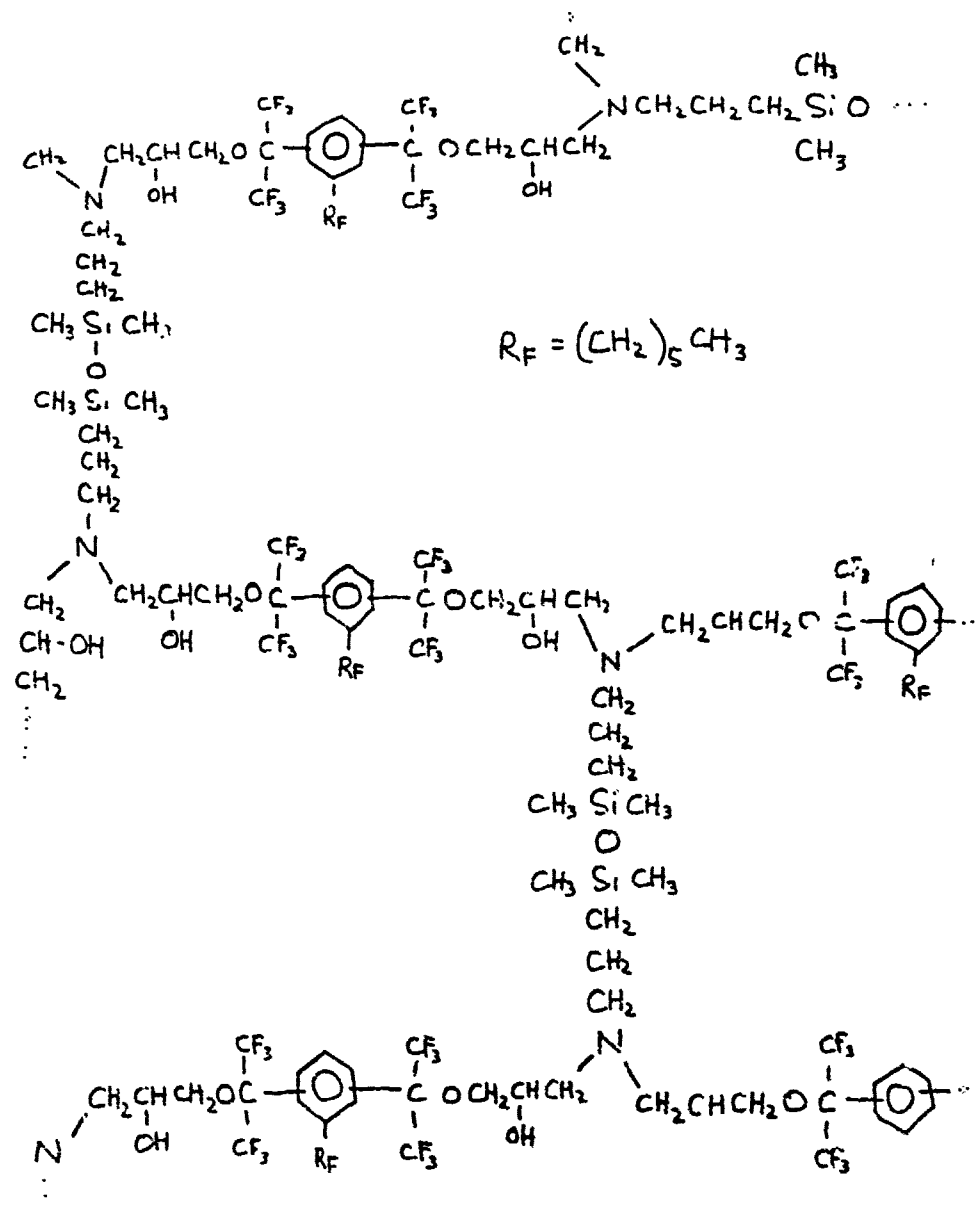


Fig. 1: Silicone Amine Cured C_6 Fluoroepoxy Resin

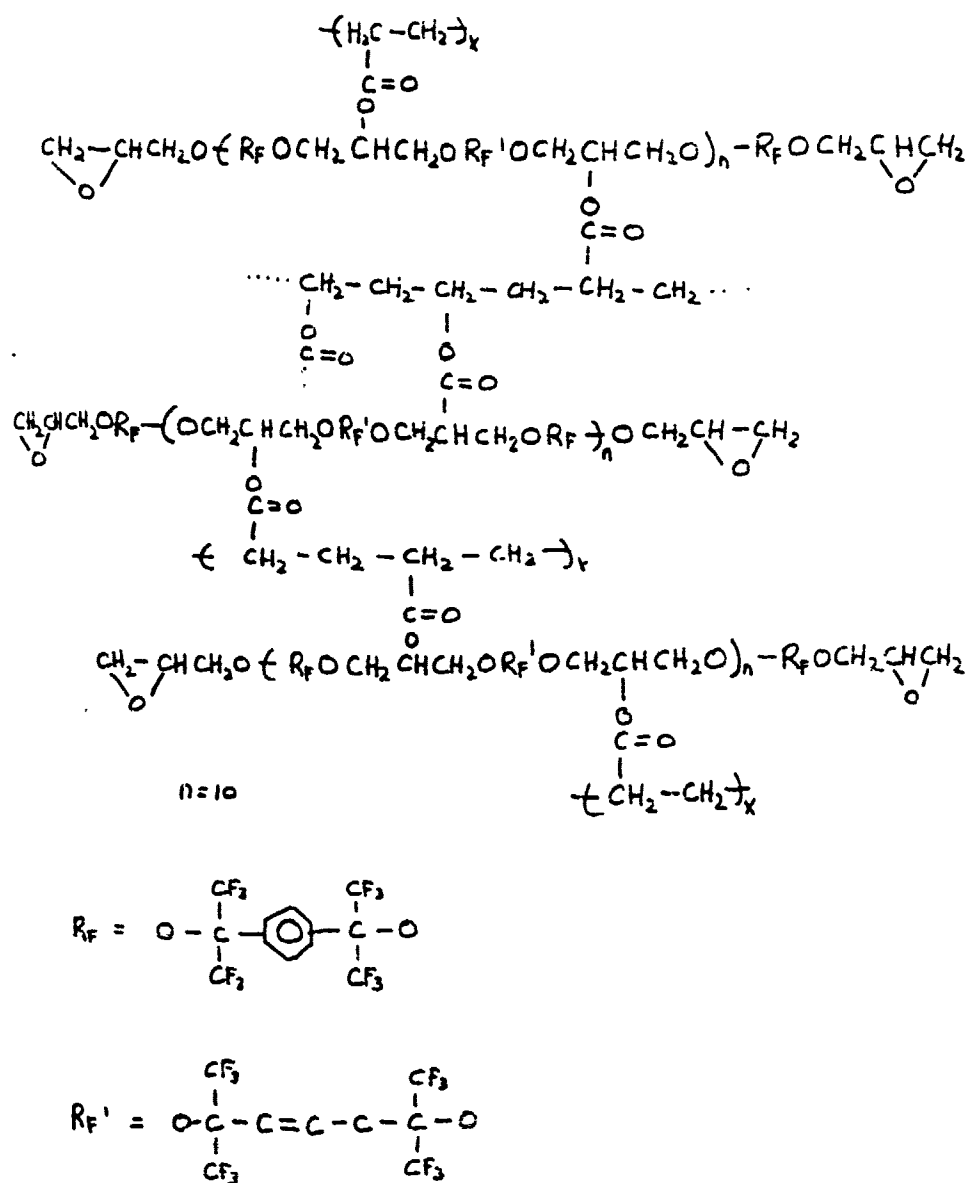


Fig. 2: Poly(fluoropolyolacrylate)

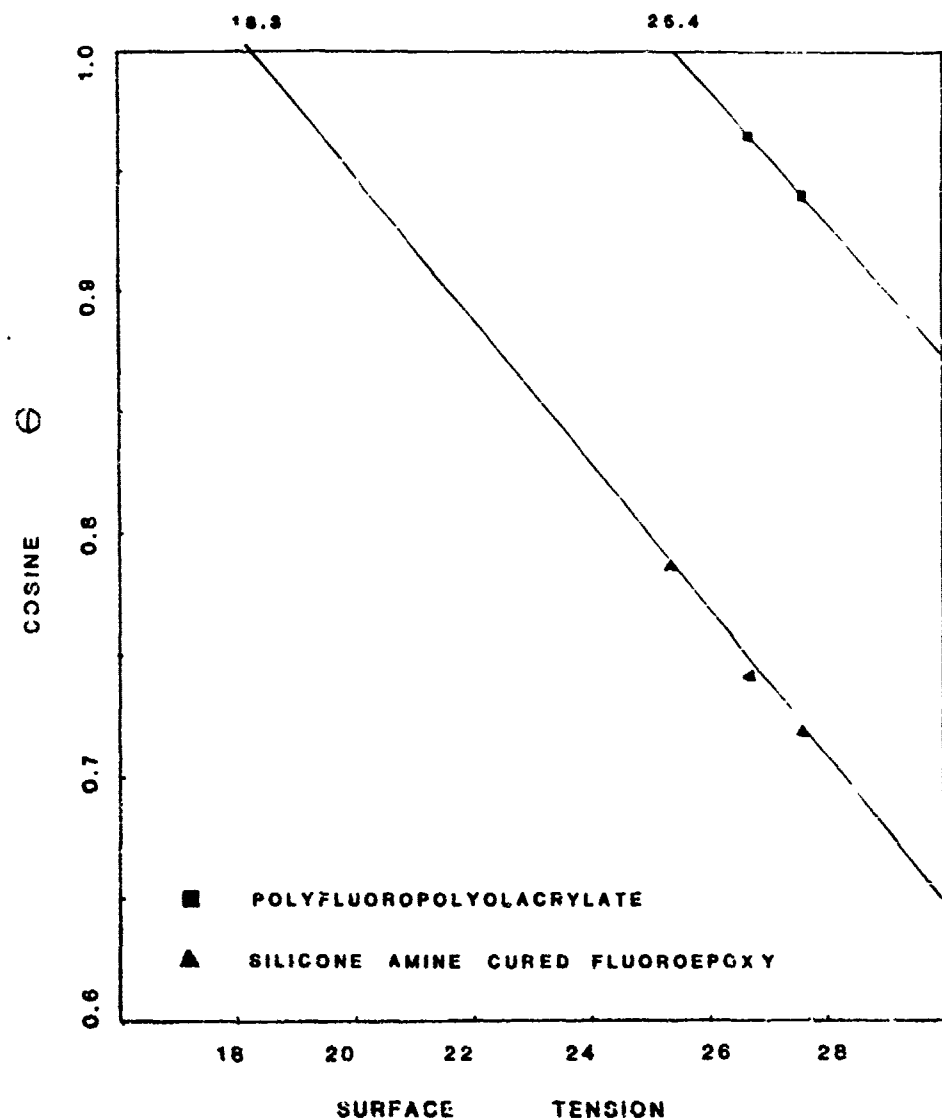


Fig. 3: Plot of Cosine θ vs. Surface Tension for N-Alkanes on Fluoroepoxy and Fluoroacrylate Polymer Films.

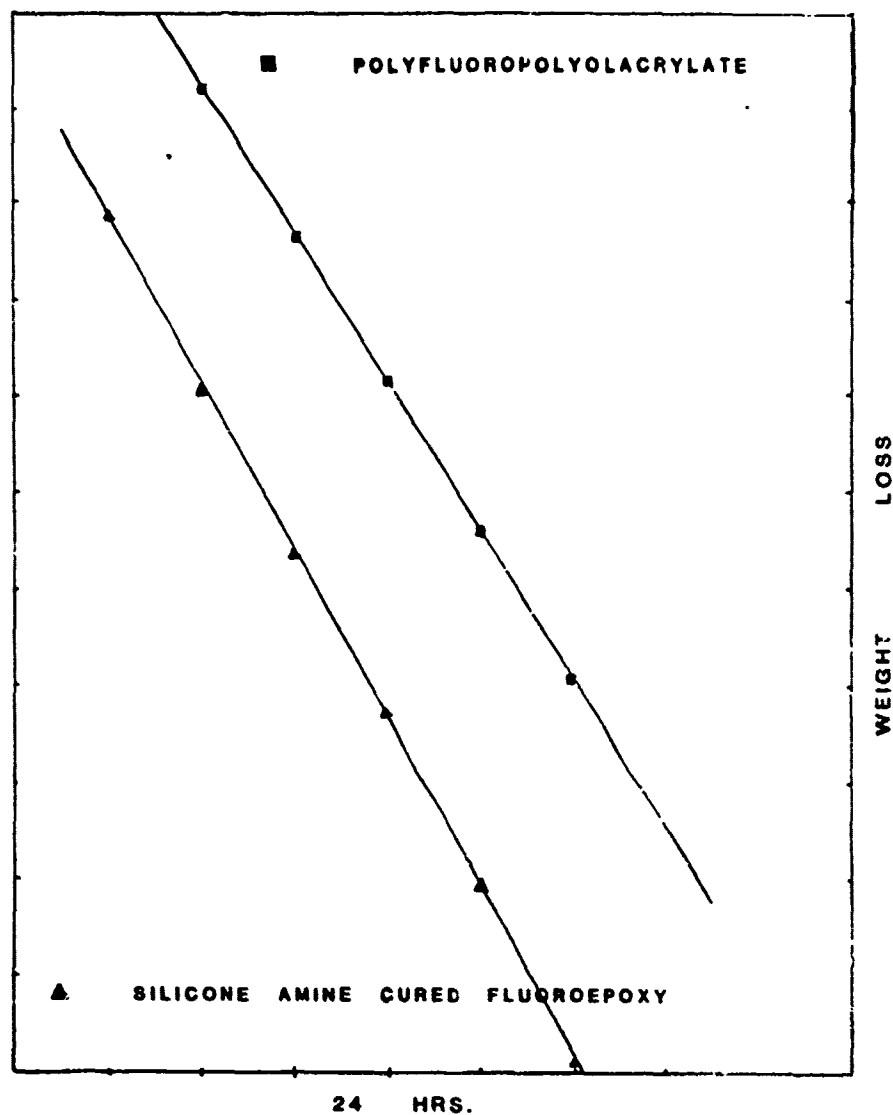


Fig. 4: Plot of Weight Loss Due to H_2O Permeation vs. 24 hr. Interval.

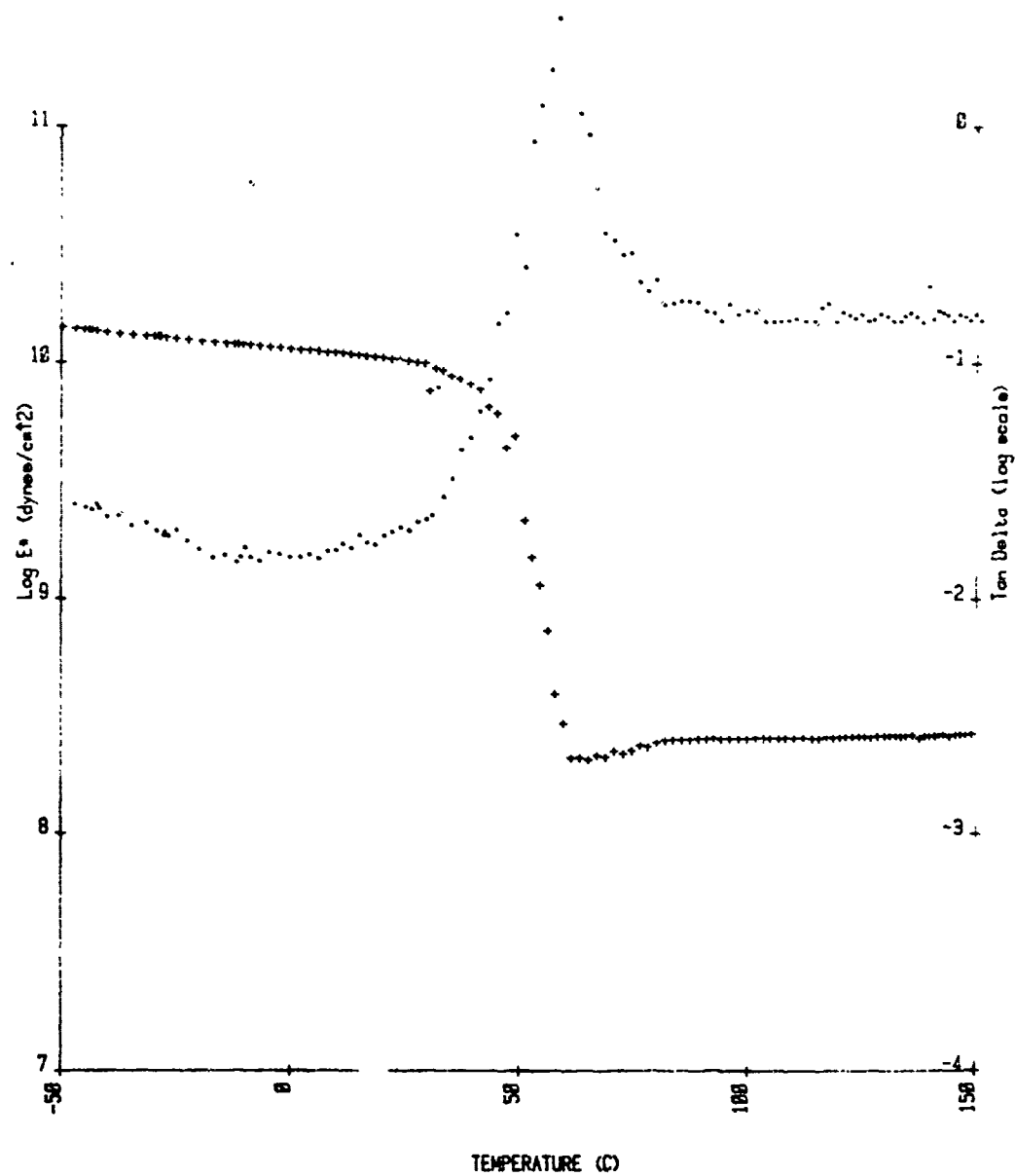


Fig. 5: The Dynamic Mechanical Properties as a Function of Temperature of Silicone Amine Cured C₆ Fluoroepoxy.

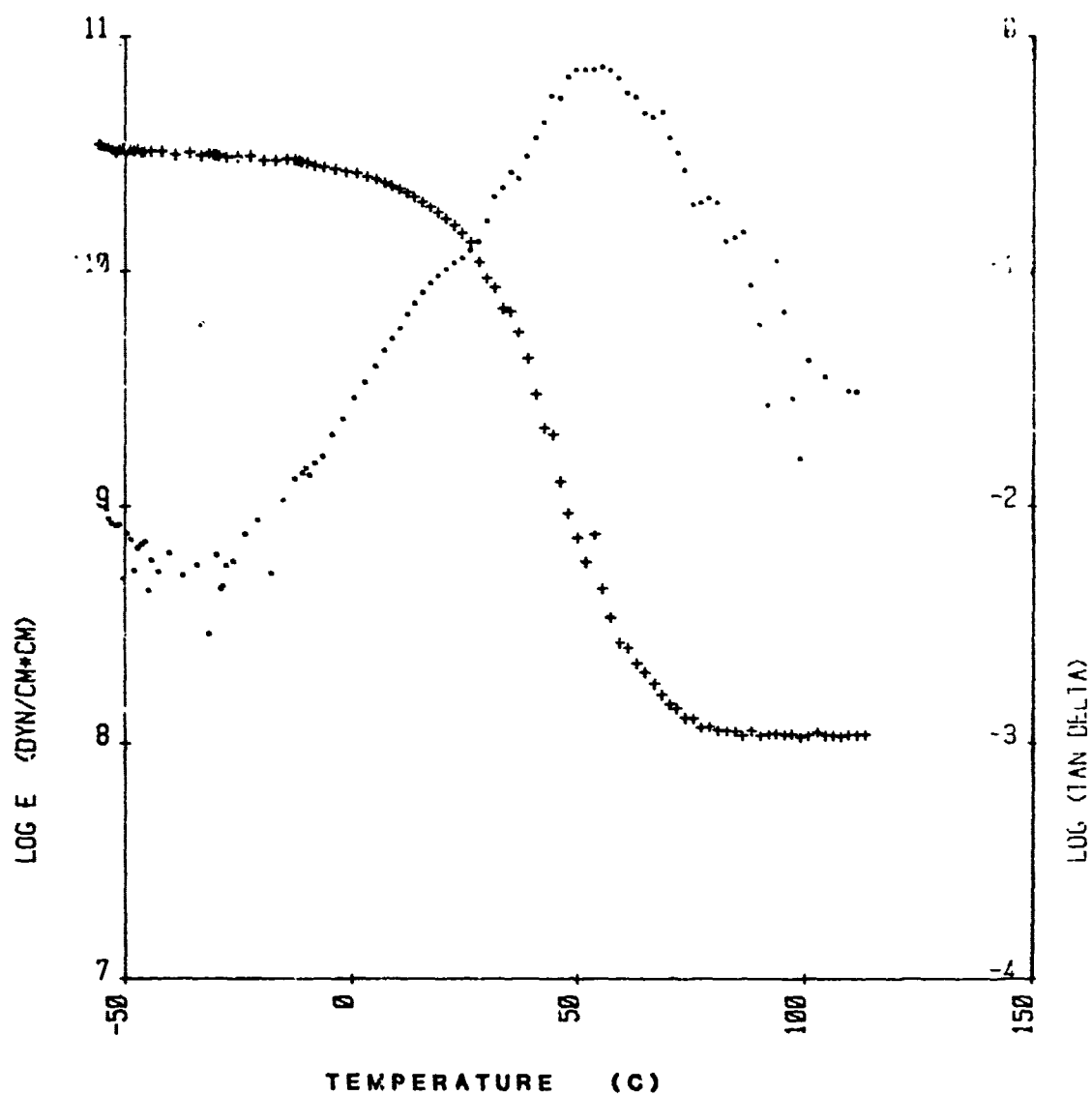


Fig. 6: The Dynamic Mechanical Properties as a Function of Temperature of Polyfluoropolyolacrylate.